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On the dissociation degree of ionic solutions considering solvation effects

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Abstract

In this work the impact of solvation effects on the dissociation degree of strong electrolytes and salts is discussed. The investigation is based on a thermodynamic model which is capable to predict qualitatively and quantitatively the double layer capacity of various electrolytes. A remarkable relationship between capacity maxima, partial molar volume of ions in solution, and solvation numbers, provides an experimental access to determine the number of solvent molecules bound to a specific ion in solution. This shows that the Stern layer is actually a saturated solution of $1\,\mathrm{mol\,L^{-1}}$ solvated ions, and we point out some fundamental similarities of this state to a saturated bulk solution. Our finding challenges the assumption of complete dissociation, even for moderate electrolyte concentrations, whereby we introduce an undissociated ion-pair in solution. We re-derive the equilibrium conditions for a two-step dissociation reaction, including solvation effects, which leads to a new relation to determine the dissociation degree. A comparison to Ostwald's dilution law clearly shows the shortcomings when solvation effects are neglected and we emphasize that complete dissociation is questionable beyond $0.5\,\mathrm{mol\,L^{-1}}$ for aqueous, mono-valent electrolytes.

Strong electrolytes and salts are frequently assumed to completely dissociate into their respective ionic species, for all concentrations up to saturation [1–6]. After Arrhenius introduced the idea of dissociation (and also incomplete dissociation) at the of the 19$^{\text{th}}$ century[7], Debye and Hückel concluded in 1923 [8] that strong electrolytes always completely dissociate in their respective ionic species [9]. From a thermodynamical point of view, this is a very strong *a priori* assumption and we show within this letter that solvation effects challenge this assumption, especially for concentrations beyond $0.5\,\mathrm{mol\,L^{-1}}$. The concept of incomplete dissociation, ion association, or formation of ion-pairs in strong electrolytes was re-introduced several times [10–13] and is again of great scientific interest [14], especially investigated by MD simulations [15, 16].

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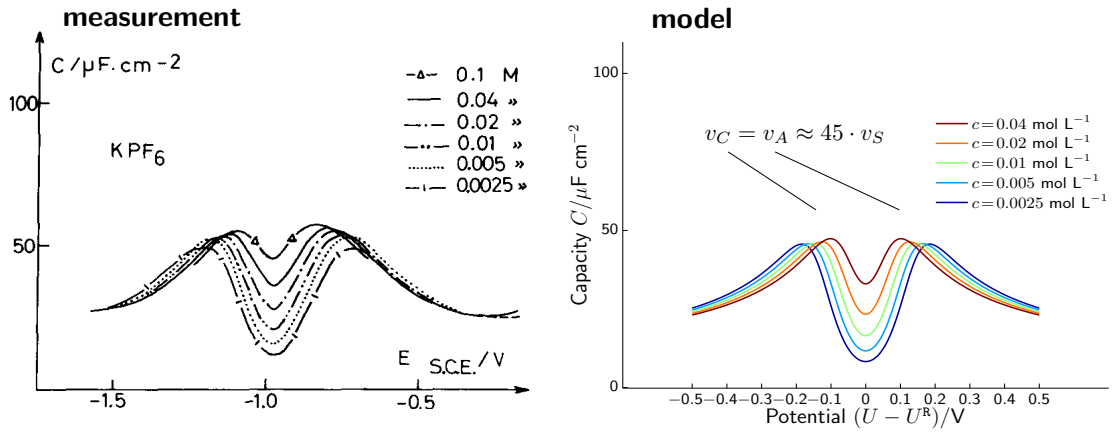

Figure 1: Comparison between measured and computed double layer capacity for a non-adsorbing and completely dissociated salt $\mathrm{KPF_6}$ (left: Fig. 2.a from [18], reprinted with permission of Elsevier)

Our investigation presented here is based on a thermodynamic model [17] which is capable to predict qualitatively and quantitatively the double layer capacity of various electrolytes (see. Fig. 1). Within a brief review of the modeling procedure, we emphasize the impact of the solvation effect on the various thermodynamic parameters. It turns out that the double layer capacity maxima are determined by the partial molar volume of the anion and the cation, respectively, whereby capacity measurements can be consulted to determine explicit values for different ions. For mono-valent ions in water we find that the partial molar volume of the ionic species is about 45 times larger than the solvent [17]. This suggests that the ionic species are strongly solvated, and based on a simple relation for the molar volume we can determine the solvation number from a single capacity measurement. A subsequent investigation of the double layer structure in the potential region beyond the capacity maximum shows the formation of an ionic saturation layer, which has some fundamental and remarkable similarities to a saturated bulk solution. This is then the starting point for our reflections on the dissociation degree, and it is shown that even for simple salts at concentrations of $(0.5 - 1)\,\mathrm{mol\,L^{-1}}$ the assumption of complete dissociation is questionable.

Consider exemplarily a mono-valent salt AC of concentration c which completely dissociates in solvated anions $\mathrm{A^-}$ and cations $\mathrm{C^+}$. Each ion $\mathrm{A^-}$ and $\mathrm{C^+}$ is assumed to bind κ_A and κ_C solvent molecules S in its solvation shell, whereby the number density of free solvent molecules S in solution is

$$n_S = n_S^{\mathrm{R}} - \kappa_A \cdot n_A - \kappa_C \cdot n_C \ . \tag{1}$$

The parameter n_S^{R} corresponds to the mole density of the liquid solvent, *i.e.* for water $n_S^{\mathrm{R}} = 55.4\,\mathrm{mol\,L^{-1}}$. The number of mixing particles is then $n = n_S + n_A + n_C$, and **not** the total number of atoms or molecules in solution, which is $n^{\mathrm{T}} = n_S^{\mathrm{R}} + n_A + n_C$. For the entropy of mixing this is extremely important. In a solvation mixture the mixing entities are now the **free** solvent molecules, the **solvated** anions and the **solvated** cations (see Fig. 2), leading to an entropy of mixing

$$s = -k_{\mathrm{B}} \left(n_S \ln\left(\frac{n_S}{n}\right) + n_A \ln\left(\frac{n_A}{n}\right) + n_C \ln\left(\frac{n_C}{n}\right)\right) \ . \tag{2}$$

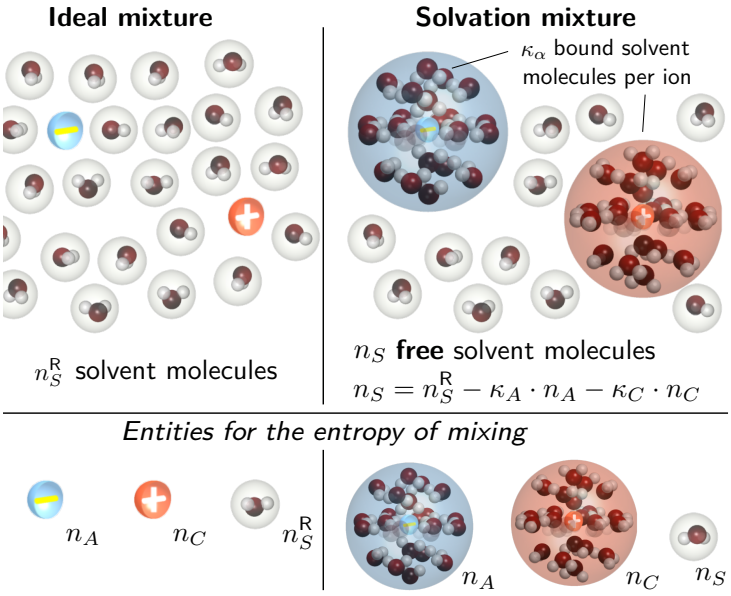

Figure 2: Sketch of solvation effect in a liquid mixture and the consequence on the entities for the entropy of mixing.

For an ideal solution, however, the mixing entities are **all** solvent molecules in addition to the dissolved ions, which gives for the entropy of mixing

$$s^{\text{ideal}} = -k_{\mathsf{B}} \left(n_S^{\mathsf{R}} \ln\left(\frac{n_S}{n^{\mathsf{T}}}\right) + n_A \ln\left(\frac{n_A}{n^{\mathsf{T}}}\right) + n_C \ln\left(\frac{n_C}{n^{\mathsf{T}}}\right) \right) \ . \tag{3}$$

Fig. 3 displays the difference between the models and shows that the impact of the solvation effect is enormous, even for small solvation numbers.

While the solvation effect decreases the number of free solvent molecules in the mixture, it actually increases the molar mass and the partial molar volume of the solvated ions. The molar mass of a solvated ion is clearly $m_{A,C} = \widetilde{m}_{A,C} + \kappa_{A,C} \cdot m_S$, where $\widetilde{m}_{A,C}$ be the mass of the central ion and m_S the molar mass of the solvent. A quite similar relation holds for the partial molar volume $v_{A,C}$ of a solvated ion. However, while the molecular mass is conserved during the solvation process, the volume is not necessarily. Bound solvent molecules may have a slightly smaller volume than in the bulk due to microscopic charge-dipole interaction which decreases their thermal motion. On the other hand, a crystal-like binding structure of the solvent molecules around the central ion may increase the volume due to less dense packing compare to the liquid state. *Ab initio* methods could probably predict precise relations between $\kappa_{A,C}$ and $v_{A,C}$ based on a microscopic structure model. But the goal of this work is not to predict such a precise relation, but rather show the general impact of the solvation effect. It is hence sufficient to assume for the partial molar volume of a solvated ion a relation

$$v_{A,C} = \widetilde{v}_{A,C} + \kappa_{A,C} \cdot v_S \quad \text{with} \quad v_S = (n_S^{\mathsf{R}})^{-1} \ , \tag{4}$$

where $\widetilde{v}_{A,C}$ is the molar volume based on the ionic radius of the respective cation and anion, v_S the molar volume of the solvent and $\kappa_{A,C}$ the solvation number. This relation allows us then to deduce a solvation number from a (measured) partial molar volume $v_{A,C}$.

The chemical potential of the free solvent, the solvated anion and the solvated cation in the

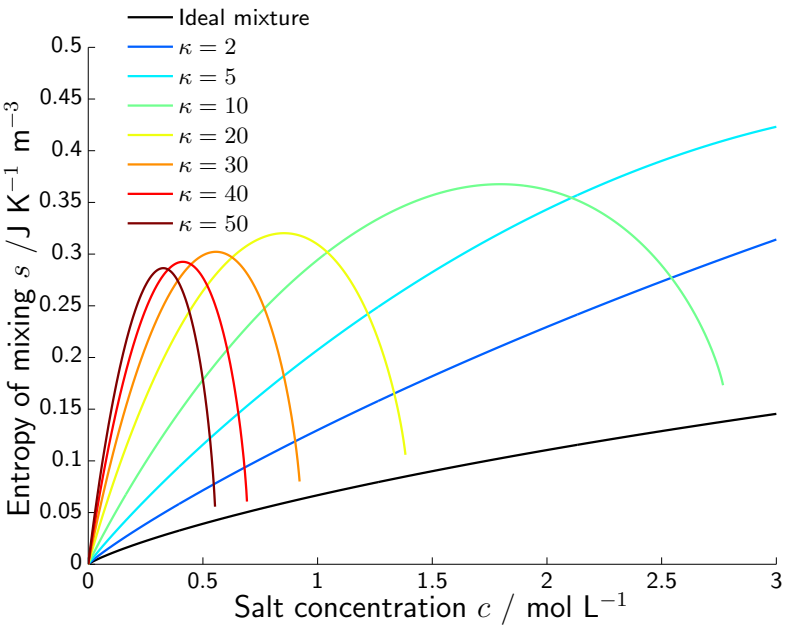

Figure 3: Entropy of mixing various solvation numbers $\kappa = \kappa_A = \kappa_C$ and an ideal mixture.

liquid, incompressible mixture is then [17]

$$\mu_\alpha = g_\alpha + k_\mathrm{B} T \ln(y_\alpha) + v_\alpha \cdot (p - p^\mathrm{E}) \qquad \alpha \in \{S, A, C\} \ , \tag{5}$$

where $y_\alpha = \frac{n_\alpha}{n}$ is the mole fraction with respect to the number density $n = n_S + n_A + n_C$ of mixing particles, g_α the constant molar Gibbs energy and p^E the bulk pressure. The corresponding incompressibility constraint reads [17]

$$v_S \cdot n_S + v_A \cdot n_A + v_C \cdot n_C = 1. \tag{6}$$

A representation of the ionic free charge density $q = e_0 \cdot (z_A n_A + z_C n_C)$ is then deduced from the flux equilibrium conditions

$$\nabla \mu_\alpha + e_0 z_\alpha \nabla \varphi = 0, \qquad \alpha \in \{S, A, C\} \ , \tag{7}$$

together with eq. (5) as

$$q = \frac{e_0 z_A \, n_A^\mathrm{E} \, \mathrm{e}^{-\frac{e_0 z_A}{k_\mathrm{B} T}\Delta\varphi - \frac{v_A}{k_B T}\Delta p} + e_0 z_C \, n_C^\mathrm{E} \, \mathrm{e}^{-\frac{e_0 z_C}{k_\mathrm{B} T}\Delta\varphi - \frac{v_C}{k_B T}\Delta p}}{v_S \, n_S^\mathrm{E} \, \mathrm{e}^{-\frac{v_S}{k_B T}\Delta p} + v_A \, n_A^\mathrm{E} \, \mathrm{e}^{-\frac{e_0 z_A}{k_\mathrm{B} T}\Delta\varphi - \frac{v_A}{k_B T}\Delta p} + v_C \, n_C^\mathrm{E} \, \mathrm{e}^{-\frac{e_0 z_C}{k_\mathrm{B} T}\Delta\varphi - \frac{v_C}{k_B T}\Delta p}}. \tag{8}$$

Here n_α^E denotes the respective bulk concentration, $\Delta p = p(x) - p^\mathrm{E}$ the pressure difference between the bulk solution and some point x (in the space charge layer), and $\Delta\varphi = \varphi(x) - \varphi^\mathrm{E}$ the electrostatic potential difference between bulk electrolyte and x. Note that the charge density remains inherently a function of the electrostatic potential $\varphi(x)$ and the material pressure $p(x)$, *i.e.* $q = q(\varphi, p)$, while almost all Poisson–Boltzmann-type approaches and recent extensions lead to representations $q = q(\varphi)$ [19–21]. For the generic case $q = q(\varphi, p)$ the Poisson equation alone is not sufficient anymore to solve the mathematical problem. But in a consistent modeling of mechanics and electrostatics in charged media one obtains actually a coupled Poisson-momentum equation system

$$-\mathrm{div}\, \varepsilon_0 (1 + \chi) \nabla \varphi = q(\varphi, p) \quad \text{and} \quad \nabla p = -q(\varphi, p) \nabla \varphi \ , \tag{9}$$

where the equation $(9)_2$ corresponds the force balance between electrostatics and mechanics [17, 22, 23]. Note that this inherent coupling is the origin of the remarkable agreement between theory and experiment on the double layer capacity (c.f. Fig. 1).

The (surface) charge stored in the electrochemical double layer is then $Q = \int_0^{x^{\mathrm{E}}} q\,dx$, where the electrode surface is positioned at $x = 0$ and the bulk electrolyte is denoted by $x = x^{\mathrm{E}}$. The equations (8) and (9) lead to an expression of Q in terms of the applied voltage $U - U^{\mathrm{R}} = \varphi|_{x=0} - \varphi^{\mathrm{E}}$, *i.e.* $Q = \hat{Q}(U)$, where U^{R} corresponds to the potential of zero charge of a non-adsorbing salt. Therewith we obtain an expression for the differential capacity $C = \frac{dQ}{dU} = \hat{C}(U)$ based on the above model which can be compared to experimental data (see Fig. 1). The continuum model shows an exceptional agreement to experimental data, an we refer to [17] for the full derivation and validation.

The capacity maxima are determined by the partial molar volume of the solvated anion and cation, respectively [17] . Surprisingly, the capacity is symmetric for many non-adsorbing salts [18, 24, 25], whereby the partial molar volumes of the anion and the cation are equal, *i.e.* $v_A \approx v_C$. The ionic volume for mono-valent salts was found to be $40 - 50$ times larger than the molar volume of the solvent, $v_{A,C} \approx (40 - 50) \cdot v_S$, which gives a radius of $r_{A,C} = \sqrt[3]{\frac{3}{4\pi} v_{A,C}} \approx (6.6 - 7.1)\,\text{Å}$ for solvated ions.

With the thermodynamic model (5)-(9) we are also able to compute the structure of the double layer for arbitrary bulk concentrations and applied voltages. It is to emphasize that this structure is obtained from the very same model which predicts the validated capacity data (Fig. 1). Fig. 4 shows a representative computation for and applied voltage of $U - U^{\mathrm{R}} = 0.5\,\mathrm{V}$ and a bulk salt concentration of $c = 0.0025\,\mathrm{mol\,L^{-1}}$. It turns out that for $U > U^{\pm}_{\mathrm{max}}$, where $U^{\pm}_{\mathrm{max}}$ denotes the potential at the capacity maxima, a saturation layer of solvated ions forms near the electrode surface. This layer grows with increasing voltage and at $U = \pm 0.5\,\mathrm{V}$ the saturation effect becomes well-marked (see Fig. 4). Note that this occurs even for very small *bulk* concentrations.

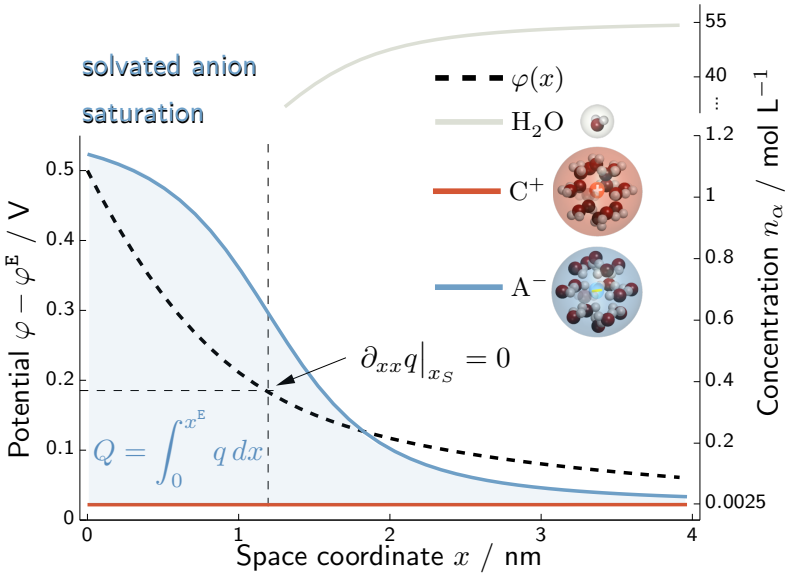

Figure 4: Computed structure of the double layer for a completely dissociated salt AC .

This saturation layer can actually be considered as the Stern layer, where the electrostatic attraction is balanced by the increased material pressure [17]. Fig. 4 shows that the saturation concentration of solvated ions is about $1\,\mathrm{mol\,L^{-1}}$. This can also be seen from the incompressibility constraint $v_S \cdot n_S + v_A \cdot n_A + v_C \cdot n_C = 1$ of the liquid mixture. For $U \to \infty$ we obtain in the Stern layer $n_S, n_A \to 0$ and thus $v_C n_C \to 1$. Since $v_C = 45 \cdot v_S \approx 0.85\,\mathrm{mol\,L^{-1}}$ we obtain directly $n_C \to 1.17\,\mathrm{mol\,L^{-1}}$. Because the saturation concentration is actually independent of the bulk concentration, it explains also why the value of the capacity maxima is almost independent of the bulk concentration. In the saturation layer the free water molecules are pushed *out* of the space charge layer in order to ensure the incompressibility of the liquid. We find that double layer is actually a saturated solution of about $1\,\mathrm{mol\,L^{-1}}$ solvated anions (or cations, respectively), based on model which precisely predicts measured capacity data. What does this imply for an electrolytic solution of $(1-2)\,\mathrm{mol\,L^{-1}}$ bulk concentration ?

The relation (4) suggest that each (mono-valent) ion solvates about $\kappa_{A,C} \approx 45$ solvent molecules. There may be some variability of this value, but it is reasonable for two solvation shells and we continue the discussion with $\kappa_{A,C} = 45$. A completely dissociated solution of $c = 0.5\,\mathrm{mol\,L^{-1}}$ AC then requires about $(\kappa_A + \kappa_C) \cdot c = 45\,\mathrm{mol\,L^{-1}}$ solvent molecules, which is almost the bulk value of water, $n_S^{\mathtt{R}} = 55.4\,\mathrm{mol\,L^{-1}}$. In this state there are not much more free solvent molecules left, which is somehow a similar state as the Stern layer. Increasing the salt concentration further would even imply a negative value of the free solvent molecules, which certainly does not occur. In consequence one has to requisition the concept of complete dissociation, even at moderate concentrations of $(0.1-1)\,\mathrm{mol\,L^{-1}}$. Note that this effect occurs also when the the solvation number is smaller, but then at little higher concentrations.

Requisitioning the concept of complete dissociation requires to state the actual bulk reactions occurring during the dissociation process. It is quite common to write the dissociation reaction of AC as

$$\mathrm{AC}\Big|^{\mathtt{R}} \rightleftharpoons \mathrm{A^-} + \mathrm{C^+} \tag{10}$$

where $^{\mathtt{R}}$ refers to the solid phase and $\mathrm{A^-}, \mathrm{C^+}$ are parts of the electrolytic mixture. However, from an elementary perspective, the process actually occurs in two steps, initially the dissolution reaction[1]

$$\mathrm{AC}\Big|^{\mathtt{R}} \rightleftharpoons \mathrm{AC} \tag{11}$$

and subsequent the dissociation reaction

$$\mathrm{AC} + (\kappa_A + \kappa_C)\mathrm{S} \rightleftharpoons \mathrm{A^-} + \mathrm{C^+}\ , \tag{12}$$

which accounts for the solvation effect. The reaction (12) implies that the constituent AC is actually a species of the liquid mixture and thus has a chemical potential in solution. Whether to term the constituent AC an ion pair, associated ion, Bjerrium pair or undissociated salt molecule in solution, is thermodynamically insignificant. What is significant, how ever, is the equilibrium condition the reaction (12) implies, namely

$$\mu_{\mathrm{AC}} + (\kappa_A + \kappa_C)\mu_S = \mu_A + \mu_C\ . \tag{13}$$

With the representation (5) of the chemical potentials μ_α, this condition actually rewrites as

$$\frac{y_A \cdot y_C}{y_{\mathrm{AC}} \cdot (y_S)^{\kappa_A+\kappa_C}} = \mathrm{e}^{\frac{\Delta g^D}{k_\mathrm{B}T}}\ , \tag{14}$$

[1] Note that this process could also require solvent molecules.

with $\Delta g^D = g_{\mathrm{AC}} + (\kappa_A + \kappa_C) \cdot g_S - g_A - g_C$. Introducing the dissociation degree δ via

$$n_A = n_C = \delta \cdot c \quad \text{and} \quad n_{\mathrm{AC}} = (1-\delta)c \,, \tag{15}$$

where c is the molar concentration of the salt, leads to

$$y_A = y_C = \frac{\delta \cdot c}{n_S^{\mathrm{R}} + 2(1-\kappa)\delta \cdot c + (1-\delta) \cdot c}, \tag{16}$$

$$y_{\mathrm{AC}} = \frac{(1-\delta) \cdot c}{n_S^{\mathrm{R}} + 2(1-\kappa)\delta \cdot c + (1-\delta) \cdot c} \,, \tag{17}$$

$$\text{and} \quad y_S = \frac{n_S^{\mathrm{R}} - 2\kappa\,\delta \cdot c}{n_S^{\mathrm{R}} + 2(1-\kappa)\delta \cdot c + (1-\delta) \cdot c} \,. \tag{18}$$

The equilibrium condition (14) is thus an algebraic constraint

$$\frac{\delta^2}{(1-\delta)} \cdot \frac{c}{n_S^{\mathrm{R}} + 2(1-\kappa)\delta \cdot c + (1-\delta) \cdot c} \cdot \left(\frac{n_S^{\mathrm{R}} + 2(1-\kappa)\delta \cdot c + (1-\delta) \cdot c}{n_S^{\mathrm{R}} - 2\kappa\,\delta \cdot c} \right)^{2\kappa} - \mathrm{e}^{\frac{\Delta g^D}{k_{\mathrm{B}} T}} = 0 \tag{19}$$

between the dissociation degree δ and the salt concentration c. The only parameters of this relation are the dissociation energy Δg^D and the solvation number $\kappa = \kappa_{A,C}$.

Since we know the solvation number $\kappa_{A,C}$ from the capacity maximum, we can numerically solve (19) for various values of Δg^D in order to determine the dissociation degree $\delta = \delta(c)$. Figure 5 shows computations of the dissociation degree from very dilute solutions up to high concentrations. Note that Ostwald's dilution law, which is frequently used to compute or approximate the dissociation degree of acids, completely ignores the solvation effect and the concept of free solvent molecules. The corresponding constraint of Ostwald's dilution law reads

$$\frac{\delta^2}{1-\delta} \cdot \frac{c}{n_S^{\mathrm{R}}} - \mathrm{e}^{\frac{\Delta g^D}{k_{\mathrm{B}} T}} = 0 \tag{20}$$

and significantly underestimates the dissociation degree, especially for higher concentrations (see comparison in Fig. 5).

For a large dissociation energy, *i.e.* $\Delta g^D > 0.1\,\mathrm{eV}$, which corresponds to a salt or a very strong electrolyte, Ostwald's dilution law predicts complete dissociation for arbitrary concentrations. In contrast, the solvation effect and its consistent incorporation in the thermodynamic theory requires incomplete dissociation beyond $0.5\,\mathrm{mol L}^{-1}$ (see Fig. 5). Origin of this effect is simply that not enough free solvent molecules are present anymore to *shift* the reaction equilibrium of (12) towards the ions in solution. For a solvation number of $\kappa_{A,C} = 45$ and a dissociation energy of $\Delta g^D = 0.1\,\mathrm{eV}$ we find that dissociation degree is $\delta = 0.99$ for $0.5\,\mathrm{mol\,L}^{-1}$, $\delta = 0.44$ for $1\,\mathrm{mol\,L}^{-1}$ and $\delta = 0.19$ for $2\,\mathrm{mol\,L}^{-1}$. Hence the assumption of complete dissociation of a salt or an electrolyte beyond a bulk concentration of $0.5\mathrm{mol\,L}^{-1}$ is questionable, and the degree of dissociation is determined by eq. (19). Surprisingly, the double layer capacity maxima are correlated to the saturation maximum (or the degree of dissociation) and represent a well defined, experimentally accessible quantity to determine the crucial parameters of the dissociation degree. Due to the solvation effect incomplete dissociation (or the formation of ion pairs) is a necessary feature for a thermodynamic consistent theory of electrolytes.

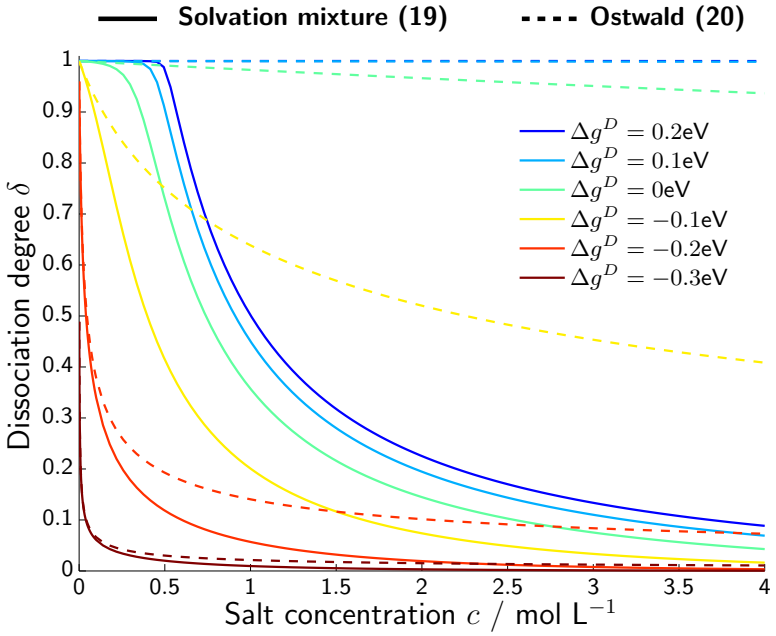

Figure 5: Comparison of the computed dissociation degree according to the solvation mixture model (19) with $\kappa = 44$ and Ostwald's dilution law (20).

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